Studies on Optical and Electrical Properties of Bis-glycine Cadmium Chloride Nonlinear Optical Single Crystazl

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Abstract: Nonlinear optical single crystals of Bis-glycine cadmium chloride (BGCC) were grown by slow evaporation technique. The unit cell dimensions and space group of the grown crystals were confirmed by single crystal X-ray diffraction analysis. The optical properties of the crystals were determined using UV-Visible absorption spectrum in the wavelength range of 200 - 900 nm. Optical constants such as band gap, extinction coefficient, refractive index, extinction coefficient and electric susceptibility were determined from UV-Visible spectroscopy. The refractive index was determined using Brewster's angle method. Second Harmonic Generation (SHG) of bis-glycine cadmium chloride crystal was investigated by Kurtz powder technique. The dielectric constant and dielectric loss measurements were carried out for different temperatures and frequencies. The photoconductivity studies confirm that the grown crystal has negative photoconductivity nature.

Keywords: Solution growth, Single X-ray diffraction, dielectric studies and photoconductivity measurement.

1. Introduction

Defect free bulk single crystals are needed for electronic industries because of their usage in the field of semiconductor, nonlinear optical (NLO), piezoelectric devices and so on. For practical applications, we need good optical transparency and also crystal should withstand high optical powers, and should have chemical stability. It is difficult to find a material that satisfies most of the above-said requirements, however, amino acid crystals are good candidates for NLO applications. Especially the complex of amino acid and strong inorganic acid plays a vital role in SHG applications. Nonlinear optics (NLO) is an innovative area of research and development which will play a key role in the field of optoelectronics and photonics [1]. The apparent development of semiorganic materials, where the organic ligand is ionically bonded with inorganic host refined the search of new materials with high optical nonlinearities which is an important area due to their optical applications such as optical communication, optical computing, optical information processing, optical disk data storage, laser fusion reaction, laser remote sensing, colour display, medical diagnostics, etc [2]. Nonlinear optical (NLO) materials play a major role in nonlinear optics and in particular they have a great impact on information technology and industrial applications. On account of the large flexibility for molecular design and higher nonlinear optical efficiency, there has been much progress in basic research on organic and semi-organic NLO materials. In this respect, amino acids are interesting materials for NLO applications [3]. Glycine forms complexes with different inorganic compounds. Some of them, e.g. triglycine sulphate [4], bisglycine manganese chloridedihydrate [5], triglycine selenate [6] and glycine silver nitrate [7], are known to have ferroelectric properties. The ferroelectric materials have a variety of functional device capabilities such as piezoelectric, actuator, nonlinear optical devices and high permittivity materials. Recently it was also reported that some of the glycine compounds like trisglycine zinc chloride also exhibit properties like SRS, SHG and THG in addition to ferroelectric properties [8]. Glycine in the zwitter ionic form also forms one dimensional chain structures and two dimensional layered structures in metal amino carboxylate coordination polymers [9]. The present investigation deal with the growth of bis-glycine cadmium chloride single crystal was grown by slow evaporation technique. The grown crystals were characterized by single crystal X-ray diffraction analysis, UV analysis, dielectric, SHG and photoconductivity measurements. The results of these studies have been discussed in this paper in detail. The optical investigations and electrical conductivity studies are carried out for grown crystal to find the suitability of the materials for device fabrications. Photoconductivity studies have also been analysed to confirm the dielectric behavior which is responsible for the induced polarization in the medium.

2. Growth of BIS-Glycine Cadmium Chloride

Slow evaporation method was employed for growing the single crystals of bis-glycine cadmium chloride. Single crystals of bis-glycine cadmium chloride were grown from glycine and cadmium chloride in the stoichiometric ratio of 3:1.The crystals were grown from aqueous solutions by slow evaporation at room temperature. The solution was stirred continuously using a magnetic stirrer. The obtained saturated solution was further purified and allowed to evaporate at higher temperature which yields powder form of the synthesized bis-glycine cadmium chloride. The recrystallized salt was used for the preparation of saturated solution at room temperature. The solution was filtered by filtration pump and Whatman filter paper of pore size 11 µm. Then the filtered solution was transferred to a petridish with a perforated lid in order to control the evaporation rate and kept undisturbed in a dust free environment. The single crystal of bis-glycine cadmium chloride of was harvested from mother solution after a growth period of 25 days.

3. Results and Discussion

3.1. Single Crystal XRD Analysis

The single crystal X-ray diffraction analysis of the grown crystals was carried out to identify the cell parameters using an ENRAF NONIUS CAD4 automatic X-ray diffractometer. The lattice parameters are estimated to be a= 8.376 Å, b= 9.082 Å, c= 13.283 Å, and hence the crystal belongs to the monoclinic system with space group Space group P21. These values are in close agreement with the reported values [10].

3.2. UV–Vis-NIR Spectral Analysis

The UV-Vis-NIR spectrum gives valuable information about the absorption of UV and visible light, which involves promotion of electrons in σ and π orbitals from the ground state to higher energy state. The optical behaviour of the material basically includes the interaction of light radiation over the range of the electromagnetic spectrum. The ultraviolet light absorbed by the sample gives information about the transparency window which is very essential in many optoelectronic applications. It is also helpful in asserting the activation energy due to electronic excitation as well as to ascertain the basic bonding present in the material. The optical absorption spectrum of bis-glycine cadmium chloride crystal shown in Fig.1 was recorded between 200 and 900 nm using PERKIN ELMER LAMDA 35 UV spectrometer. The lower cut-off wavelength of bis-glycine cadmium chloride was found to be at 250 nm. The band gap of the crystal was estimated from the relation in equation (1)

$$E_g = \frac{1.243\times 10^3}{\lambda_{\max}} \quad (1)$$

The band gap value was found to be 4.97 eV which is typical of dielectric materials. The wide energy band gap shows that the defect concentration in the grown crystals is very low and large transmittance in the visible region. The very low absorptions of the grown crystals in the entire visible region is due to the delocalization of electronic cloud through charge transfer axis and suggests its suitability for second harmonic generation and other related optoelectronic applications [11,12].

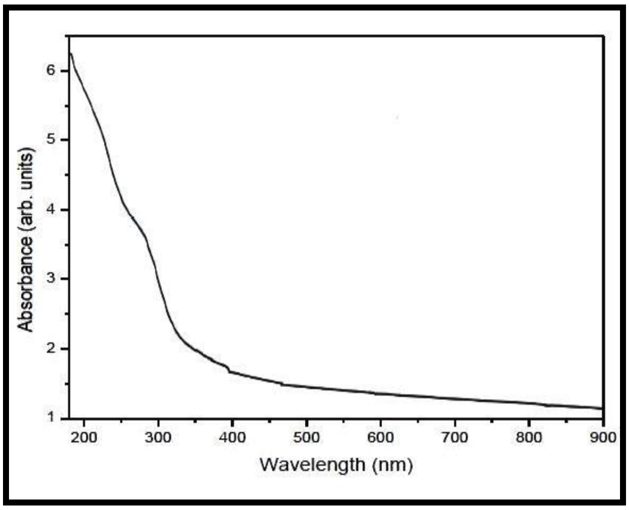

Fig.1 Absorption spectrum of bis-glycine cadmium chloride

3.2.1. Determination of optical constants

Two of the most important optical properties; refractive index (n) and the extinction coefficient (K) are generally called optical constants. The amount of light that transmitted through materials depends on the amount of the reflection and absorption that takes place along the light path. The optical constants such as the refractive index (n), the real dielectric constant(εr) and the imaginary parts of dielectric constant (εi) respectively.The extinction coefficient (K) can be obtained from the following equation,

$$K = \frac{\lambda\alpha}{4\pi} \quad (2)$$

The extinction coefficient (K) was found to be 5.12 x 10-6 at λ =900 nm. The transmittance (T) is given by

$$T = \frac{(1-R)^2 \exp(-\alpha t)}{1-R^2 \exp(-2\alpha t)} \quad (3)$$

Reflectance (R) in terms of absorption coefficient can be obtained from the above equation. Hence,

$$R = \frac{1 \pm \sqrt{1-\exp(-\alpha t + \exp(\alpha t)}}{1+\exp(-\alpha t)} \quad (4)$$

Refractive index (n) can be determined from reflectance data using the following equation,

$$n = -\frac{(R+1) \pm \sqrt{3R^2 + 10R - 3}}{2(R-1)} \tag{5}$$

The refractive index (n) was found to be 1.863 at λ =900 nm. From the optical constants, electric susceptibility (χc) can be calculated according to the following relation [13]

$$\varepsilon_r = \varepsilon_0 + 4\pi\chi_C = n^2 - k^2 \tag{6}$$

Hence,

$$\chi_C = \frac{n^2 - k^2 - \varepsilon_0}{4\pi} \tag{7}$$

where ε_0 is the permittivity of free space. The value of electric susceptibility χ_C is 0.175 at λ =900 nm. The real part dielectric constant ε_r and imaginary part dielectric constant ε_i can be calculated from the following relations [14]

$$\varepsilon_r = n^2 - k^2$$

$$\varepsilon_i = 2nk \tag{8}$$

The value of real ε_r and ε_i imaginary dielectric constants at λ =900 nm were estimated as 1.782 and 5.707 x 10-5 , respectively. The moderate values of refractive index and optical band gap suggest that the material has the required transmission range for NLO application. The lower value of dielectric constant and the positive value of the material are capable of producing induced polarization due to intense incident light radiation.

3.3. Refractive Index Measurements

Finely polished crystals of the as grown bis-glycine cadmium chloride were used for refractive index measurements. These crystals were cleaved and are placed on a rotating mount at an angle varying from 0 to 90 degrees. He-Ne laser of wavelength 632.8 nm was used as the source. Brewster's angle (θp) for bis-glycine cadmium chloride was measured to be 61.17 degree. The refractive index has been calculated using the equation n = tan θp, where θp is the polarizing angle and it is found to be 1.816.

3.4. NLO Test – Kurtz Powder SHG Method

The most widely used technique for confirming the SHG efficiency of NLO materials to identify the materials with non-centrosymmetric crystal structures is the Kurtz Powder technique [15]. Fine powders of bis-glycine cadmium chloride crystals were exposed under 1064 nm laser beam from a pulsed Nd:YAG laser having a repetition rate of 10 Hz and pulse width of 8 ns to test the second harmonic generation (SHG) efficiency. The SHG output 532 nm (green light) was finally detected by the photomultiplier tube. The powdered material of potassium dihydrogen phosphate (KDP) was used in the same experiment as a reference material. The output power intensity of bis-glycine cadmium chloride was found to be 1.5 times that of KDP.

3.5. Dielectric Studies

Dielectric properties are related with the electric field distribution within solid materials. This is a normal dielectric behaviour that both dielectric constant and dielectric loss decrease with increase in frequency. Dielectric studies were carried out using a HIOKI LCR HITESTER in the frequency range from 50 Hz to 5 MHz. A crystal of having silver coating on the opposite faces was placed between the two copper electrodes and a parallel plate capacitor was thus formed. The capacitance of the crystal was measured by varying the frequency from 50Hz to 5 MHz and the graph is plotted between dielectric constant Vs logarithmic frequency is (Fig. 2). Fig. 2 shows the variation of the dielectric constant with log frequency at different temperatures. From the plot, it is observed that the dielectric constant is relatively higher in the region of 50Hz-5MHz and decreases further with an increase in the frequency, and this trend continues up to 5 MHz. After this, the dielectric constant remains almost constant at all other higher frequencies. The high value of the dielectric constant at low frequency is due to the presence of electronic, ionic, dipolar and space charge polarizations [16]. In accordance with the Miller rule, the lower value of the dielectric constant at higher frequencies is a suitable parameter for the enhancement of the SHG coefficient [17]. The variation of the dielectric loss with frequency is shown in Fig.3. The characteristic of a low dielectric loss with high frequency for the crystal suggests that the crystal possesses enhanced optical quality with lesser defects and this parameter plays a vital role in the fabrication of nonlinear optical devices [18].

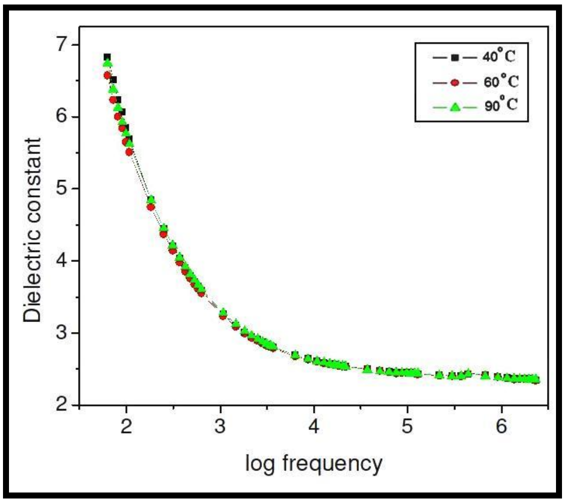

Fig. 2. Variation of dielectric constant with log frequency

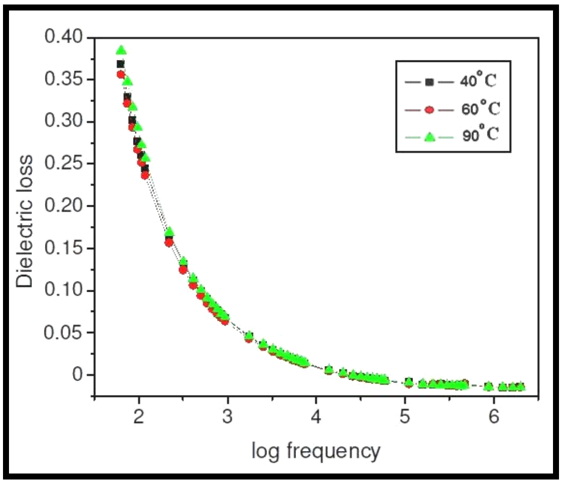

Fig. 3. Variation of dielectric loss with log frequency

3.6. Photoconductivity Studies

Photoconductivity measurements were carried out on a cut and polished sample of the bis-glycine cadmium chloride grown single crystal by fixing it onto a microscope slide. The crystal was connected in series with a DC power supply and KEITHLEY 485 Picoammeter. The crystal was then exposed to light radiation and the photocurrent was recorded for the same values of the applied voltage. The decrease in lifetime with illumination could be due to the trapping process and increase in carrier velocity according to the relation,

$$\tau = (\nu s N)^{-1} \tag{9}$$

where v is the thermal velocity of the carriers, s is the capture cross-section of the recombination centers and N is the carrier concentration. As intense light falls on the sample, the lifetime of the characterization decreases. In the Stockmann model, a two level scheme is proposed to explain negative photoconductivity [19]. As a result, the recombination of electrons and holes takes place resulting in decrease in the number of mobile charge carriers, giving rise to negative photoconductivity. Fig.4 shows the variation of both dark and photocurrent with applied field. The dark current and photocurrent increases linearly with respect to the applied field. At every instant, the dark current is greater than the photocurrent, which is due to the negative photoconductivity. This may be attributed to the decrease in either the number of free charge carriers or their lifetime when subjected to radiation. According to the Stockmann model, the forbidden gap in the material contains two energy levels in which one is situated between the Fermi level and the conduction band, while the other is located close to the valence band. The second state has high capture cross-sections for electrons and holes. As it captures electrons from the conduction band and holes from the valence band, the number of charge carriers in the conduction bands gets reduced, and the current decreases in the presence of radiation. Thus the crystal is said to exhibit a negative photoconducting effect. The negative photoconductivity of the bis-glycine cadmium chloride may be due to the reduction in the number of charge carriers to reveal the dielectric nature of the material.

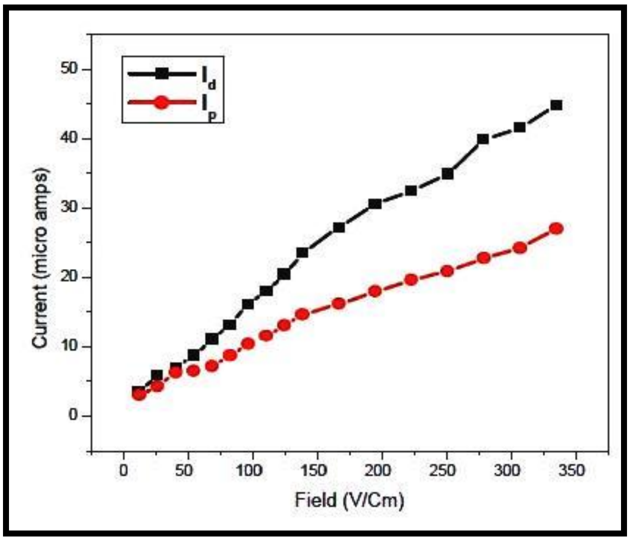

Fig. 4. Photoconductivity study of bis-glycine cadmium chloride crystal.

4. Conclusion

Single crystal of Bis-glycine cadmium chloride was grown by the slow evaporation technique. The single crystal XRD analysis confirms that the crystal belongs to the monoclinic system. The UV-Visible absorption spectrum shows excellent transmission in the entire visible region. The optical constants such as optical band gap, extinction coefficient, refractive index, electric susceptibility and dielectric constants were calculated to analyze the optical property. Second Harmonic Generation (SHG) efficiency of the bis-glycine cadmium chloride is greater than KDP. The dielectric constant and dielectric loss were studied as a function of frequency at different temperatures. The photoconductivity studies confirm that the crystal possesses negative photoconductivity nature.

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